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DETERMINATION OF DIFFERENCES AND RATIOS OF

SPECIFIC HEATS AND CHANGE IN ENTROPY

AS APPLIED TO FIVE EQUATIONS OF STATE FOR GASES

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**U S ARMY MISSILE COMMAND**
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DETERMINATION OF DIFFERENCES AND RATIOS OF

SPECIFIC HEATS AND CHANGE IN ENTROPY

AS APPLIED TO FIVE EQUATIONS OF STATE FOR GASES

By

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## ABSTRACT

Presented in this report are the results of an investigation to determine analytically two thermodynamic transport properties -- difference in specific heats and the change in entropy -- as described by five independent equations of state for gases.

Change in entropy and specific heats of gases are used in thermodynamics work to evaluate properties of gases undergoing change of state such as flow properties behind shocks. Change of entropy is a logical starting point for this work and where applicable properties are known at high temperatures these equations may be used.

Steam was used for illustrative purposes because it is a well defined, thoroughly explored gas.

The development of the equations precedes each equation in a logical, straightforward manner and ends with the desired properties in terms of known thermodynamic coordinates.

Comparison of the calculated change in entropy is presented in bar-graph form in Figures 1 and 2 for these equations of state for a real gas, superheated steam. A comparison of the difference in specific heats for these equations for the same gas is given in Figure 3.

In both the entropy change and the difference in specific heat, good agreement is found among the five equations of state.

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## I.    INTRODUCTION

The purpose of this report is to determine the difference in specific heats at constant pressure and constant volume, the ratio of these two, and the change in entropy for five equations of state. These are the perfect gas, Callendar, Dieterici, Berthelot, and Van der Waals equations. After these relations have been established, some examples of how they might be used will be shown for superheated steam.

## II.    DISCUSSION

It is desirable to obtain the difference in specific heat at constant pressure and the specific heat at constant volume for a substance in terms of pressure, volume, and temperature.

Heat capacity may be defined as the ratio of heat entering the system and the change in temperature of the system or substance. The instantaneous heat capacity, or specific heat, is defined as this ratio as both the heat added and temperature change become smaller and smaller. Written in mathematical terms, $C = \dfrac{dQ}{dT}$ . This has a unique value when the pressure or volume of a substance is kept constant; thus, $C_p = \left(\dfrac{dQ}{dT_p}\right)$ and $C_v = \left(\dfrac{dQ}{dT_v}\right)$ . This requires, then, that specific heat be a function of at least two variables in thermodynamics.

For two reversible paths joining two equilibrium states of a system from Clausius' theorem we may write:

$$\int_{R_1 R_2} \frac{dQ}{dT} = 0 \quad \text{or} \quad \int_{R_1}{}_i^f \frac{dQ}{T} + \int_{R_2}{}_f^i \frac{dQ}{T} = 0,$$

where $R_1$ and $R_2$ refer to the path taken from and to points i and f in any thermodynamic system.

$$-\int_{R_2}{}_f^i \frac{dQ}{T} = \int_{R_1}{}_i^f \frac{dQ}{T} = \int_{R_2}{}_i^f \frac{dQ}{T}$$

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which means that $\int_i^f \frac{dQ}{T}$ is independent of the path taken and allows a function to exist in the coordinates of the system whose final value minus the value at the initial points equals the integral $_R\int_i^f \frac{dQ}{T}$ . We may call it the entropy. If the two states are made infinitesimally near, the integral may be dropped and the difference replaced by the differential. Therefore, $\frac{dQ_r}{T} = ds$ . It is interesting to note that although dQ is not an exact differential, ds is exact. The reciprocal of the Kelvin temperature is the integrating factor. Dividing both sides by dT and multiplying by T gives $\frac{dQ}{dT} = \frac{Tds}{dT}$ . If we restrict this expression to constant volume and constant pressure, respectively, we get:

$$\left(\frac{dQ}{dT}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v \quad ; \quad \left(\frac{dQ}{dT}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p$$

To show entropy as a function of two thermodynamic variables, we will use the following two theorems in mathematics.

Theorem 1. If a relation exists among x, y, and z, we may imagine z expressed as a function of x and y; whence,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy.$$

If we let:

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x \quad ; \text{ then, } dz = M \, dx + N \, dy,$$

where z, M, and N are all functions of x and y. Differentiating M partially, with respect to y, and N with respect to x, we get:

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \, \partial y}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \, \partial x} \quad .$$

Since the two second derivatives on the right are equal, it follows that:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad .$$

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This is known as the condition for an exact differential.

Theorem 2. If quantity f is a function of x, y, and z, and a relation exists among x, y, and z; then f may be regarded as a function of any two of x, y, and z. Similarly, any one of x, y, and z may be considered to be a function of f and one other of x, y, and z. Thus, regarding x to be a function of f and y,

$$dx = \left(\frac{\partial x}{\partial f}\right)_y \ df + \left(\frac{\partial x}{\partial y}\right)_f \ dy.$$

Considering y to be a function of f and z,

$$dy = \left(\frac{\partial y}{\partial f}\right)_z \ df + \left(\frac{\partial y}{\partial z}\right)_f \ dz.$$

Substituting this expression for dy in the preceding equation, we get:

$$dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z \right] df + \left[\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \right] dz.$$

But, $$dx = \left(\frac{\partial x}{\partial f}\right)_z \ df + \left(\frac{\partial x}{\partial z}\right)_f \ dz.$$

Equating the dz terms of the last two equations, we get:

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f = \left(\frac{\partial x}{\partial z}\right)_f \ , \ \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1.$$

It may be shown that $\left(\frac{dQ}{dT}\right)_v = C_v$ and $\left(\frac{dQ}{dT}\right)_P = C_p.$

To arrive at the difference in specific heats in the pressure, volume, and temperature coordinates we may use entropy as a function of T and V, and T and P, respectively.

$$ds = \left(\frac{\partial s}{\partial T}\right)_v \ dT + \left(\frac{\partial s}{\partial v}\right)_T \ dv. \ \text{Multiplying through by}$$

$$T, \ Tds = T\left(\frac{\partial s}{\partial T}\right)_v \ dT + T\left(\frac{\partial s}{\partial v}\right)_T \ dv = C_v \ dT + T\left(\frac{\partial s}{\partial v}\right)_T \ dv.$$

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From the equation of the Helmholtz function $A = U - Ts$, we get the differential resulting in an infitesimal change. $dA = dU - Tds - sdT = -pdv - sdT$, this is an exact differential since A is an actual function. From the above mathematical theorems we see that $-\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$. Now:

$$Tds = Cv\, dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

Imagining entropy to be a function of T and p we obtain: $ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$. Multiplying through by T,

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp = Cp\, dT + T\left(\frac{\partial s}{\partial p}\right)_T dp.$$

From the change in Gibbs function, $G = H - Ts$, $dG = dH - Tds - sdT$ $dG = vdp - sdT$, an exact differential. Therefore, so now

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \qquad Tds = Cp\, dT + T\left(\frac{-\partial v}{\partial T}\right)_p dp$$

$$Tds = Cp\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp.$$

Equating these two equations: $Tds = Cp\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$

$$Tds = Cv\, dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

$Cp\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp = Cv\, dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$ ; solving for

dT, $Cp\,dT - Cv\,dT = T\left(\frac{\partial v}{\partial T}\right)_p dp + T\left(\frac{\partial p}{\partial T}\right)_v dv$

$dT = \frac{T}{Cp-Cv}\left(\frac{\partial v}{\partial T}\right)_p dp + \frac{T}{Cp-Cv}\left(\frac{\partial p}{\partial T}\right)_v dv$. Imagining T to

be a function of V and p, $dT = \left(\frac{\partial T}{\partial v}\right)_p dv + \left(\frac{\partial T}{\partial p}\right)_v dp$

so $\left(\frac{\partial T}{\partial v}\right)_p dv + \left(\frac{\partial T}{\partial p}\right)_v dp = \frac{T}{Cp-Cv}\left(\frac{\partial v}{\partial T}\right)_p dp + \frac{T}{Cp-Cv}\left(\frac{\partial p}{\partial T}\right)_v dv$.

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Therefore, the terms corresponding to dv and dp on each side of the equation are equal.

$$\left(\frac{\partial T}{\partial v}\right)_p = \frac{T}{C_p - C_v} \left(\frac{\partial p}{\partial T}\right)_v \quad \text{and} \quad \left(\frac{\partial T}{\partial P}\right)_v = \frac{T}{C_p - C_v} \left(\frac{\partial v}{\partial T}\right)_p$$

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \quad \text{and} \quad C_p - C_v = T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$$

which, of course, is the same from each equation.

To show clearly that $C_p - C_v$ is always positive for all known substances let us get the change in pressure with respect to volume instead of $\left(\frac{\partial p}{\partial T}\right)_v$ in this equation.

To do this let us use the two mathematical theorems discussed earlier. Suppose a relationship exists between pressure, P, volume, V, and temperature, T, so that $f(P, V, T) = 0$. Let us imagine P as a function of v and T.

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT \quad \text{and } v \text{ as a function of } p \text{ and } T.$$

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT \quad \text{and } v \text{ as a function of } p \text{ and } T.$$

$$dv = \left(\frac{\partial v}{\partial P}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT$$

$$dp = \left(\frac{\partial p}{\partial v}\right)_T \left[ \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT \right] + \left(\frac{\partial p}{\partial T}\right)_v dT$$

$$= \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial p}{\partial T}\right)_v dT$$

$$dp = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T dp + \left[ \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial p}{\partial T}\right)_v \right] dT.$$

Now, of the three coordinates only two are independent. Let us choose p and T as the independent coordinates. The above equation must be true for all values of dp and dT. First, let us make dT = 0, and dp not equal 0.

Then, $dp = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T \cdot dp + 0$ or $\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T = 1$

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If dp = 0 and dT not equal 0 then,

$$0 = \frac{(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial p}_T \ 0 + \left[ \frac{(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial T}_p + \frac{(\partial p)}{\partial T}_v \right] dT,$$

so then, the coefficient of dT must equal 0.

$$\frac{(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial T}_p + \frac{(\partial p)}{\partial T}_v = 0 \quad ; \quad \frac{(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial T}_p = \frac{-(\partial p)}{\partial T}_v$$

$$\frac{(\partial p)}{\partial T}_v = \frac{-(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial T}_p \quad ; \quad \text{substituting this relation into}$$

the specific heat difference equation we get:

$$Cp-Cv = T \frac{(\partial p)}{\partial T}_v \ \frac{(\partial v)}{\partial T}_p = T \left[ - \frac{(\partial p)}{\partial v}_T \ \frac{(\partial v)}{\partial T}_p \right] \frac{(\partial v)}{\partial T}_p$$

$$Cp-Cv = -T \frac{(\partial v)^2}{\partial T}_p \ \frac{(\partial p)}{\partial vT}$$

First of all, it may be remembered that $\frac{(\partial p)}{\partial v}_T$ is always

negative for any known substance so the two negative signs when multiplied will give a positive. T will always be

positive and $\frac{(\partial v)}{\partial T_p}$ is squared, and, whether positive or

negative, the square will be positive. Therefore, Cp-Cv will always be positive, or Cv is never greater than Cp.

It may be noted that as T approaches absolute zero the

heat capacities are equal. Cp may equal Cv when $\frac{(\partial v)}{\partial T}_p = 0$

as in the case of water at maximum density. Next, we may determine the ratio of specific heat as a function of P, T, and V.

From the two Tds equations derived previously,

$$Tds = CpdT - T \frac{(\partial v)}{\partial T_p} dp \quad ; \quad Tds = CvdT + T \frac{(\partial p)}{\partial T_v} dv$$

at constant entropy ds = 0 and $CpdT = T \frac{(\partial v)}{\partial T_p} dp$

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$$CvdT = -T \frac{(\partial p)}{\partial T}_v \, dv \quad ; \quad \text{divide second into first}$$

$$\frac{Cp}{Cv} = -\frac{(\partial v)}{\partial T}_p \frac{(\partial T)}{\partial p}_v \frac{(\partial p)}{\partial v}_s \quad ; \quad \text{but from the mathematical}$$

theorems we may rearrange our second term of

$$\frac{(\partial p)}{\partial v}_T \frac{(\partial v)}{\partial T}_p + \frac{(\partial p)}{\partial T}_v = 0 \qquad \text{to get an equality for}$$

$$\left[ \frac{(\partial v)}{\partial T}_p \frac{(\partial T)}{\partial p}_v \right] \quad ; \quad \frac{(\partial p)}{\partial v}_T \frac{(\partial v)}{\partial T}_p = - \frac{(\partial p)}{\partial T}_v \quad ;$$

$$\frac{(\partial T)}{\partial p}_v \frac{(\partial p)}{\partial v}_T \frac{(\partial v)}{\partial T}_p = -1 \quad ; \quad \frac{(\partial v)}{\partial T}_p \frac{(\partial T)}{\partial p}_v = - \frac{(\partial v)}{\partial p}_T \, .$$

Substituting in the specific heat ratio $\frac{Cp}{Cv}$ equation we get:

$$\frac{Cp}{Cv} = -\frac{(\partial v)}{\partial T}_p \frac{(\partial T)}{\partial p}_v \frac{(\partial p)}{\partial v}_s = - \left[ - \frac{(\partial v)}{\partial p}_T \right] \frac{(\partial p)}{\partial v}_s =$$

$$\frac{(\partial v)}{\partial p}_T \frac{(\partial p)}{\partial v}_s \quad \text{or} \quad \frac{Cp}{Cv} = \frac{(\partial v)}{\partial p}_T \frac{(\partial p)}{\partial v}_s \, .$$


There is possibly another relationship between
P, V, and T for entropy so that the fundamental Tds equation
might be used for $\frac{Cp}{Cv}$ , where an identity might be obtained
for $\frac{(\partial p)}{\partial v}_s$ . This may be accomplished by using a fundamental
mathematical theorem which will relate entropy (s) to
pressure (P), volume (V), and temperature (T). It is known
that entropy is a function of p, v, and T and that a
relationship exists among p, v, and T so that entropy may
be regarded as a function of any two of p, v, and T.
Similarly, any one of p, v, and T may be considered a
function of entropy and one other of p, v, and T. Thus,

regarding p to be a function of s and v,

$$dp = \frac{(\partial p)}{\partial s}_v \, ds + \frac{(\partial p)}{\partial v}_s \, dv \quad ; \quad \text{and considering v to be a}$$

function of s and T, $dv = \left(\frac{\partial v}{\partial s}\right)_T ds + \left(\frac{\partial v}{\partial T}\right)_s dT$ ; substituting

this expression for dv into the former equation:

$$dp = \left(\frac{\partial p}{\partial s}\right)_v ds + \left(\frac{\partial p}{\partial v}\right)_s \left[\left(\frac{\partial v}{\partial s}\right)_T ds + \left(\frac{\partial v}{\partial T}\right)_s dT\right]$$

$$dp = \left(\frac{\partial p}{\partial s}\right)_v ds + \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T ds + \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_s dT$$

$$dp = \left[\left(\frac{\partial p}{\partial s}\right)_v + \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T\right] ds + \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_s dT \; .$$

Equating the dT terms of the equations for dp we get:

$$dp = \left(\frac{\partial p}{\partial s}\right)_T ds + \left(\frac{\partial p}{\partial T}\right)_s dT$$

$$dp = \left[\left(\frac{\partial p}{\partial s}\right)_v + \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T\right] ds + \left[\left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_s\right] dT$$

$$\left(\frac{\partial p}{\partial T}\right)_s = \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_s \qquad \text{or} \qquad 1 = \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_s$$

$$\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial T}{\partial v}\right)_s \qquad \text{so} \qquad \frac{Cp}{Cv} = \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial T}{\partial v}\right)_s$$

From the equation of the difference in specific heats, we will obtain the relationships of p, v, T and other constants for three types of gases. The first will be the ideal gas equation. $pv = RT$

$$Cp-Cv = - T \left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T \qquad \left(\frac{\partial v}{\partial T}\right)_p^2 = \left(\frac{\partial \frac{RT}{p}}{\partial T}\right)_p^2 = \frac{R^2}{p^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = - \frac{RT}{v^2} \; ; \; Cp-Cv = - T \frac{R^3}{p^2} \; \frac{-T}{v^2} = \frac{R^3 \; T^2}{p^2 \; v^2}$$

but $\frac{R^2 \; T^2}{p^2 \; v^2} = 1$  and  $Cp-Cv = R$ for <u>an ideal gas.</u>

Next we will get the difference in specific heats for a gas that follows the <u>Van der Waals equation of state.</u>

$$(P + \frac{a}{v^2}) (v-b) = RT \; ; \; T = \frac{1}{R} (p + \frac{a}{v^2}) (v-b)$$

$$\frac{(\partial T)}{\partial v}_p = \frac{1}{R} \left[ (p + \frac{a}{v^2}) + (v-b) \frac{(-2a)}{v^3} \right] \; ; \; \text{squaring this term}$$

we get: $\frac{1}{R^2} \left[ (p + \frac{a}{v^2}) - (v-b) \frac{(2a)}{v^3} \right]^2$ ; inverting this

we obtain: $\dfrac{(\partial v)^2}{\partial T}_p = \dfrac{R^2}{\left[ p + \dfrac{a}{v^2} - \dfrac{2a(v-b)}{v^3} \right]^2}$

$$\frac{(\partial p)}{\partial V}_T = \frac{2a}{v^3} - \frac{RT}{(v-b)^2} = \frac{2a (v-b)^2 - RTv^3}{v^3 (v-b)^2} = - \left[ \frac{RTv^3 - 2a(v-b)^2}{v^3 (v-b)^2} \right]$$

$$Cp-Cv = -T \frac{(\partial v)^2}{\partial T}_p \frac{(\partial p)}{\partial v}_T$$

$$Cp-Cv = \left[ \frac{TR^2}{\left[ P + \dfrac{a}{v^2} - \dfrac{2a(v-b)}{v^3} \right]^2} \right] \left[ \frac{RTv^3 - 2a (v-b)^2}{v^3 (v-b)^2} \right]$$

$$= R^2T \left[ \frac{1}{\left[ P + \dfrac{a}{v^2} - \dfrac{2a (v-b)}{v^3} \right]^2} \right] \left[ \frac{RT v^3 - 2a(v-b)^2}{v^3(v-b)^2} \right]$$

Van der Waals' equation.

The difference in specific heat for a gas that obeys the <u>Callendar equation of state:</u>

$$RT = p(v-b + \frac{a}{T^n}) \quad \text{where } n = \frac{10}{3}$$

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$$\left(\frac{\partial v}{\partial T}\right)_p = \left[\frac{\partial\left(\frac{RT}{p} - \frac{a}{T^n} + b\right)}{\partial T}\right]_p = \frac{R}{p} + \frac{na}{T^{n+1}}$$

$$\left(\frac{\partial v}{\partial T}\right)_p^2 = \left[\frac{R}{p} + \frac{na}{T^{n+1}}\right]^2 ; \quad \left(\frac{\partial p}{\partial v}\right)_T = \frac{(v-b + \frac{a}{T^n})\ 0\ -\ RT}{(v-b + \frac{a}{T^n})^2}$$

$$Cp-Cv = -T\ \left(\frac{\partial v}{\partial T}\right)_p^2\ \left(\frac{\partial p}{\partial v}\right)_T = T\ \left[\frac{R}{p} + \frac{na}{T^{n+1}}\right]^2\ \left[\frac{RT}{(v-b + \frac{a}{T^n})^2}\right]$$

$$= RT^2 \left[\frac{RT^{n+1} + pna}{p\,T^{n+1}\ (v-b + \frac{a}{T^n})}\right]^2 \quad ; \quad \text{where } n = \frac{10}{3}\ ;\ n + 1 = \frac{13}{3}$$

$$\therefore\ Cp-Cv = RT^2 \left[\frac{RT^{\frac{13}{3}} \cdot p^{\frac{10}{3}}\ a}{p\,T\ (v-b + \frac{a}{T^{\frac{10}{3}}})}\right]^2 \qquad \text{Callendar's equation.}$$

## Berthelot's equation of state:

$$p = \frac{RT}{v-b}\ \frac{-a}{Tv^2} \qquad \text{or} \qquad \frac{RT}{v-b}\ -\ \frac{a}{Tv^2}\ -\ p = 0$$

$$Cp-Cv = -T\left(\frac{\partial v}{\partial T}\right)_p^2\ \left(\frac{\partial p}{\partial v}\right)_T$$

$$\left(\frac{\partial p}{\partial v}\right)_T = \left[\frac{\partial\left(\frac{RT}{v-b}\ \frac{-a}{Tv^2}\right)}{\partial v}\right]_T = \frac{-RT}{(v-b)^2}\ +\ \frac{2a}{Tv^3}$$

$$\left[\frac{\partial\left(\frac{RT}{v-b}\ \frac{-a}{Tv^2}\ -\ p\right)}{\partial T}\right]_p = \left[\frac{\partial\left(\frac{RT}{v-b}\right)}{\partial T}\right]_p\ -\ \frac{\partial\left(\frac{a}{Tv^2}\right)}{\partial T}\Big|_p\ -\ \left[\frac{\partial p}{\partial T}\right]_p = 0$$

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$$0 = \frac{(v-b)R - RT\left(\frac{dv}{dT}\right)_p}{(v-b)^2} - \frac{(Tv^2)\,0 - a\left[T^2v\left(\frac{dv}{dT}\right)_p + v^2\right] - 0}{(Tv^2)^2} = 0$$

$$0 = \frac{R(v-b) - RT\left(\frac{dv}{dT}\right)_p}{(v-b)^2} + \frac{2aT\,v\left(\frac{dv}{dT}\right)_p + av^2}{(Tv^2)^2}$$

$$0 = \frac{RT^2v^4(v-b) - RT^3v^4\left(\frac{dv}{dT}\right)_p + 2aTv(v-b)^2\left(\frac{dv}{dT}\right)_p + av^2(v-b)^2}{T^2v^4(v-b)^2}$$

$$RT^2v^4(v-b) - RT^3v^4\left(\frac{dv}{dT}\right)_p + 2aTv(v-b)^2\left(\frac{dv}{dT}\right)_p + av^2(v-b)^2 = 0$$

$$RT^2v^4(v-b) + av^2(v-b)^2 = \left(\frac{dv}{dT}\right)_p\left[RT^3v^4 - 2aTv(\dot{v}-b)^2\right]$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT^2v^4(v-b) + av^2(v-b)^2}{RT^3v^4 - 2aTv(v-b)^2}$$

$$\left(\frac{\partial v}{\partial T}\right)_p^2 = \left[\frac{RT^2v^4(v-b) + av^2(v-b)^2}{RT^3v^4 - 2aTv(v-b)^2}\right]^2 = \left[\frac{RT^2v^3(v-b) + av(v-b)^2}{RT^3v^3 - 2aT(v-b)^2}\right]^2$$

$$Cp-Cv = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T$$

$$Cp-Cv = -T\left[\frac{RT^2v^3(v-b) + av(v-b)^2}{RT^3v^3 - 2aT(v-b)^2}\right]^2 \left[\frac{-RT}{(v-b)^2} + \frac{2a}{Tv^3}\right]$$

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$$Cp-Cv = \left[\frac{RT^2 \quad (v-b) + a/v^2(v-b)^2}{RT^3 \quad \dfrac{-2aT(v-b)^2}{v^3}}\right]^2 \left[\frac{RT^2}{(v-b)^2} + 2a\frac{2a}{v^3}\right] =$$

$$\frac{T \left[\dfrac{R}{v-b} + \dfrac{a}{T^2v^2}\right]^2}{\left[\dfrac{-2a}{Tv^3} + \dfrac{RT}{(v-b)^2}\right]}$$

<u>Dieterici equation of state:</u> $\quad p = \dfrac{RT}{(v-b)} e^{\left(\frac{-a}{RTv}\right)}$

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\left(\frac{\partial}{\partial v} \quad \frac{(RT \ e^{\frac{-a}{RTv}}}{v-b}\right)\right)_T = RT\left[\frac{(v-b)e^{\frac{-a}{RTv}}\frac{a}{(RTv^2)} - e^{\frac{-a}{RTv}}}{(v-b)^2}\right]$$

$$\left(\frac{\partial p}{\partial v}\right)_T = RTe^{\frac{-a}{RTv}}\left[\frac{(v-b)(\frac{a}{RTv^2}) - 1}{(v-b)^2}\right] = RTe^{\frac{-a}{RTv}}\left[\frac{a}{RTv^2(v-b)} - \frac{1}{(v-b)^2}\right]$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial \frac{(RTe^{\frac{-a}{RTv}}}{v-b}}{\partial T}\right)_p + \left(\frac{\frac{(RT}{\partial v-b}e^{\frac{-a}{RTv}})}{\partial v}\right)_p$$

$$= \frac{\dfrac{R}{v-b}\left[T \ e^{\frac{-a}{RTv}} \ \dfrac{a}{(RvT^2)} + e^{\frac{-a}{RTv}}\right]}{RT\left[\dfrac{(v-b) \frac{a}{RTv^2} \ e^{\frac{-a}{RTv}} - e^{\frac{-a}{RTv}}}{(v-b)^2}\right]}$$

$$= \cdot \frac{\frac{a}{RvT} + 1}{\frac{T(v-b)}{(v-b)^2}\left[(v-b)\ \frac{a}{RTv^2} - 1\right]} = \frac{v-b\ \left[\frac{a}{RvT} + 1\right]}{T\ \left[(v-b)\frac{a}{RTv^2} - 1\right]}$$

$$= \frac{\frac{a}{RTv} + 1}{T\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]} \quad ; \quad \frac{(\partial v)^2}{\partial T}\ p = \left[\frac{1 + \frac{a}{RTv}}{T\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]}\right]^2$$

$$Cp-Cv = \frac{-\left[1 + \frac{a}{RTv}\right]^2}{T\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]^2}\left[RTe^{\frac{-a}{RTv}}\left\{\frac{a}{RTv^2(v-b)} - \frac{1}{(v-b)^2}\right\}\right]$$

$$= \frac{\left[1 + \frac{a}{RTv}\right]^2}{\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]^2}\left[\frac{1}{(v-b)^2} - \frac{a}{RTv^2\ (v-b)}\right]Re^{\frac{-a}{RTv}}$$

Using properties of superheated steam from a point near the saturated line to a point far away from the saturated line, we may compare the values of these three expressions for the difference in specific heats.

The first to be calculated will be the idèal gas case. This is a constant and is equal to the universal gas constant. The universal gas constant is approximately 1545 ft lb/lb mol°R. Cp-Cv = 1545 ft lb/lb mol°R for the ideal gas.

To solve for the two constants we will employ the properties of the critical isotherm at the intersection of the saturation line for the Van der Waals, Berthelot, and Dieterici equations. For the callendar equation, we will choose two points in the superheated steam range of values to obtain these constants. This is done because the Callendar equation does not apply at the critical point.

### Berthelot's equation:

Since the critical point is the limiting position as two points on each of the saturated liquid and the saturated

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vapor at the same pressure and temperature approach each other, it follows that at a maximum point on the curve, the slope is zero. This means that $\left(\frac{\partial p}{\partial v}\right)_T = 0$; also, since the critical point is a point of inflection on the critical isotherm, $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$.

From these two facts, plus the equations themselves, we may determine the two constants.

Berthelot's equation: $p = \frac{RT}{v-b} - \frac{a}{Tv^2}$

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial \frac{RT}{v-b}}{\partial v}\right)_T - \left(\frac{\partial \frac{a}{Tv^2}}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} - \left(-\frac{2a}{Tv^3}\right) = \frac{2a}{Tv^3} - \frac{RT}{(v-b)^2}$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = -\frac{6a}{Tv^4} + \frac{2RT}{(v-b)^3} = 0 = \frac{2a}{Tv^3} - \frac{RT}{(v-b)^2}$$

$$\frac{6a}{Tv^4} = \frac{2RT}{(v-b)^3} \quad ; \quad \frac{2a}{Tv^3} = \frac{RT}{(v-b)^2} \qquad \frac{3a}{Tv^4} = \frac{RT}{(v-b)^3}$$

Dividing one by the other, we eliminate a and obtain b, in terms of the critical volume.

$$\frac{2aTv^4}{Tv^3\,3a} \cdot \frac{RT(v-b)^3}{(v-b)^2\,RT} = v-b = \frac{2}{3}v$$

$$v-\frac{2}{3}v = b; \text{ or } v_c = \frac{b}{3}$$

Putting this into the first equation we get:

$$\frac{2a}{T(3b)^3} = \frac{RT}{(3b-b)^2} \quad ;$$

$$\frac{2a}{T(3b)^3} = \frac{RT}{4b^2} = \frac{2a}{T27b^3} \qquad T^2 = \frac{2a4b^2}{27b^3R} = \frac{8a}{27bR}$$

or $T_c = \sqrt{\dfrac{8a}{27bR}}$ ; and putting these two values into the equation we obtain:

$$P_c = \frac{R\sqrt{\dfrac{8a}{27bR}}}{3b-b} - \frac{a}{\sqrt{\dfrac{8a}{27bR}}\,(3b)^2} = \sqrt{\frac{8aR}{27b}}\,\frac{1}{2b} - \frac{a}{\sqrt{\dfrac{8a}{27bR}}\,9b^2}$$

$$= \sqrt{\frac{8aR}{27b^3 x^4}} - \frac{1}{\sqrt{\dfrac{8 \times 81b^4}{27abR}}} = \sqrt{\frac{2aR}{27b^3}} - \frac{1}{\sqrt{\dfrac{24b^3}{aR}}}$$

$$\frac{\sqrt{\dfrac{20R24b^3}{27b^3aR}} - 1}{\sqrt{\dfrac{24b^3}{aR}}} = \frac{\sqrt{\dfrac{48}{27}} - 1}{\sqrt{\dfrac{24\,b^3}{aR}}} = \frac{\dfrac{1}{3}}{\sqrt{\dfrac{24\,b^3}{aR}}}$$

$$P_c = \frac{1}{3}\sqrt{\frac{aR}{24b^3}} = \frac{1}{b}\sqrt{\frac{aR}{24 \times 9b}} = \frac{1}{b}\sqrt{\frac{2aR}{\frac{3\times3}{2}(24\times9)b}} = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$$

$$P = \frac{RT}{v-b}\,e^{\frac{-a}{RTv}} ; \quad \left(\frac{\partial p}{\partial v}\right)_T = \frac{RT}{(v-b)}e^{\frac{-a}{RTv}}\,\frac{a}{RTv^2} + e^{\frac{-a}{RTv}} - \frac{RT}{(v-b)^2}$$

$$e^{\frac{-a}{RTv}}\left[\frac{RT}{(v-b)}\,\frac{a}{RTv^2} - \frac{RT}{(v-b)^2}\right] = \frac{e^{\frac{-a}{RTv}}\,RT}{(v-b)}\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right] = 0$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{RTe^{\frac{-a}{RTv}}}{v-b} \left[\frac{-2a}{RTv^3} + \frac{1}{(v-b)^2}\right] + \left[\frac{a}{RTv^2} - \frac{1}{v-b}\right] RT$$

$$\left[\frac{(v-b)e^{\frac{-a}{RTv}}\left(\frac{a}{RTv^2}\right) - e^{\frac{-a}{RTv}}}{(v-b)^2}\right]$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{RTe^{\frac{-a}{RTv}}}{v-b}\left[\frac{1}{(v-b)^2} - \frac{2a}{RTv^3}\right] + RT\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]$$

$$\left[e^{\frac{-a}{RTv}}\frac{\left(\frac{(v-b)\,a}{RTv^2} - 1\right)}{(v-b)^2}\right]$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{RTe^{\frac{-a}{RTv}}}{v-b}\left\{\left[\frac{1}{(v-b)^2} - \frac{2a}{RTv^3}\right] + \left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]\left[\frac{(v-b)a}{(v-b)RTv^2} - \right.\right.$$

$$\left.\left.\frac{1}{(v-b)^2}\right]\right\} = \frac{RT\,e^{\frac{-a}{RTv}}}{v-b}\left\{\left[\frac{1}{(v-b)^2} - \frac{2a}{RTv^3}\right] + \left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]\right.$$

$$\left.\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]\right\} = \frac{RTe^{\frac{-a}{RTv}}}{v-b}\left\{\left[\frac{1}{(v-b)^2} - \frac{2a}{RTv^3}\right] + \left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]^2\right\} = 0$$

$$\frac{a}{RTv^2} = \frac{1}{v-b} \quad ; \quad \frac{1}{(v-b)^2} - \frac{2a}{RTv^3} = \left[\frac{a}{RTv^2} - \frac{1}{v-b}\right]^2$$

$$a = \frac{RTv^2}{v-b}\frac{1}{(v-b)^2} - \frac{2\,RTv^2}{(v-b)\,RTv^3} = \left[\frac{RTv^2}{(v-b)V^2RT} - \frac{1}{v-b}\right]^2$$

$$\frac{1}{(v-b)^2} - \frac{2}{(v-b)}v = \left[\frac{1}{v-b} - \frac{1}{v-b}\right]^2 = 0$$

$$\frac{1}{(v-b)^2} = \frac{2}{(v-b)v} \quad ; \quad \frac{(v-b)v}{(v-b)^2} = 2 = \frac{v}{v-b}$$

$$2v-2b = v \quad ; \quad 2v-v = 2b \quad ; \quad \underline{\underline{v = 2b}} \ .$$

Substituting this back into the first equation for derivative

we get: $\dfrac{a}{RT(2b)^2} - \dfrac{1}{2b-b} = 0$

$$\frac{a}{RT4b^2} = \frac{1}{b} \quad \frac{ab}{R4b^2} = \quad Tc = \frac{a}{4Rb}$$

Substituting these answers back into the equation of state
we find:

$$Pc = \frac{Ra\ e^{-\frac{a4Rb}{Ra2b}}}{4Rb(2b-b)} = \frac{ae^{-2}}{4b^2} = \frac{a}{4\ e^2b^2} = Pc$$

## Van der Waals' equation of state:

$$\left(P +\frac{a}{v^2}\right)\left(_{v-b}\right) = RT \qquad or \qquad P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \qquad \frac{2a}{v^3} = \frac{RT}{(v-b)^2}$$

$$\frac{\partial^2 p}{\partial v^2}\ _T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \qquad \frac{3a}{v^4} = \frac{RT}{(v-b)^3}$$

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$$\frac{2av^4}{v^3 3a} = \frac{RT}{(v-b)^2} \frac{(v-b)^3}{RT} = \frac{2}{3} \; v = v-b$$

$$v - \frac{2}{3} v = b = \frac{1}{3} vc \quad ; \quad \frac{2a}{(3b)^3} = \frac{RT}{(3b-b)^2} = \frac{2a}{27b^3} = \frac{RT}{4b^2}$$

$$\frac{2a}{27b} = \frac{RT}{4} \quad ; \quad Tc = \frac{8a}{27Rb}$$

Finally, substituting into the equation of state we get:

$$Pc = \frac{8a}{27b(2b)} - \frac{a}{9b^2} = \frac{4a-3a}{27b^2} = \frac{a}{27b^2} = Pc$$

Since the Callendar equation of state does not apply at the critical point, we may obtain the approximate values of its constants by substituting values of P, T, and v in the superheated steam range where this equation is applicable.

Point one will be a pressure of 40 psia, a temperature of 300°F, and v = 11.04 ft$^3$/lb specific volume. The first point will be p = 80 psia; T = 500°F; and v = 7.02 ft$^3$/lb.

$$a = (-v + b + \frac{RT}{p}) T^n = (-126.2 + b + \frac{1545 \times 960}{11,520})(.96)^{\frac{10}{3}} \times 10^{10}$$

$$a = 873 \times 10^7 \; (b + 128.5 - 126.2) = 873 \times 10^7 \; (b + 2.3)$$

$$b = \frac{873 \times 10^7 \; (b + 2.3)}{401 \times 10^7} - 4.8 = \frac{873}{401} b + \frac{873(2.3)}{401} - 4.8$$

$$2.175b - b = 4.8 - 5 = - 0.2 = 1.175b$$

$$b = -.17 ft^3/lbmol$$

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Using another point of p, v, and T we find:

a,b, p = 160 psia, T = 900°F, v = 5.015 ft$^3$/lb

$$a = (-v + b + \frac{RT}{p})T^n = (-90 + b + \frac{1545 \times 136.0}{23,050})(1.36)^{\frac{10}{3}} \times 10^{10}$$

$$a = (b + 91.1 - 90)\ 2.781 \times 10^{10} = (b + 1.1)\ 2.781 \times 10^{10}$$

Equating these two we get: $(b + 1.1)\ 2.781 \times 10^{10} =$

$(b + 2.3).873 \times 10^{10}$; $(b + 1.1)\ \frac{2.781}{.873} = b + 2.3$ ; $\frac{2.781}{.873}b +$

$$\frac{1.1(2.791)}{0.873} = b + 2.3$$

$$3.185b - b = 2.3 - 3.5$$

$$2.185b = -1.2 \qquad \underline{\underline{b = -0.55}} \qquad \text{Callendar's equation.}$$

$$a = (b + 1.1)\ 2.781 \times 10^{10} = (1.1 - 0.55)\ 2.781 \times 10^{10} = \underline{\underline{1.53 \times 10^{10}}}$$

For the <u>Berthelot equation of state for steam:</u>

$v_c$ = 0.906 ft$^3$/lbmol $\qquad p_c$ = 459,000 lb/ft$^2$

$T_c$ = 705°F = 1165°R

$$b = \frac{v_c}{3} = \frac{0.906}{3} = 0.302\ \text{ft}^3/\text{lbmol}$$

$$(12b\ p_c)^2 = \frac{2Ra}{3b} \quad ; \quad a = \frac{3b(12bp_c)^2}{2R} = \frac{(.906)(4(.906)4.59)^2 \times 10^{10}}{2 \times 1545}$$

$$a = \frac{(.906)\ 278 \times 10^{10}}{3.09 \times 10^3} = 81.4 \times 10^7 = 8.14 \times 10^8\ \frac{\text{lb}}{\frac{\text{ft}^2(\text{ft}^3)^2\ °R}{\text{lbmol}}}$$

$$a = 8.14 \times 10^8 \frac{(ft^3)^2}{lbmol} \quad °R \frac{lb}{ft^2}$$

Calculation of Cp-Cv for <u>Berthelot equation</u> at point one,

$p = 1440$ psfa, $T = 660°R$

$v = 700$ ft$^3$/lbmol

$$a = 8.14 \times 10^8 \frac{(ft^3)^2}{(lbmol)^2} \quad \frac{°Rlb}{ft^2} \quad b = 0.302 \frac{ft^3}{lbmol}$$

<u>Berthelot's equation:</u>

$$Cp-Cv = T \frac{\left[\dfrac{R}{v-b} + \dfrac{a}{T^2 v^2}\right]^2}{\dfrac{RT}{(v-b)^2} - \dfrac{2a}{Tv^3}} =$$

$$\frac{6.6 \times 10^2 \left[\dfrac{1545}{700-.302} + \dfrac{8.14 \times 10^8}{(6.6)^2 \times 49^2 \times 10^4}\right]^2}{\dfrac{1545 \times 660}{(700-.302)^2} - \dfrac{2(8.14)(10^8)}{(660)343 \times 10^6}}$$

$$Cp-Cv = 660 \frac{[2.207143 + 0.00381]^2}{2.081 - 0.00719}$$

$$Cp-Cv = 1556$$

<u>Dieterici's equation of state:</u>

$p = 1440$ psfa ; $T = 660°R$, $v = 700 \dfrac{ft^3}{lbmol}$

$a = 3.2 \times 10^6$ ; $b = 0.453$

$$Cp-Cv = \frac{Re^{\frac{-a}{RTv}}\left[1 + \dfrac{a}{RTv}\right]^2}{\left[\dfrac{a}{RTv^2} - \dfrac{1}{v-b}\right]^2} \quad \left[\dfrac{1}{(v-b)^2} - \dfrac{a}{RTv^2(v-b)}\right]$$

$$Cp-Cv = \cfrac{1.545 \times 10^3 \quad e^{\cfrac{-3.2 \times 10^6}{1.545 \times 10^3 \times .66 \times 10^3 \times 7. \times 10^2}}}{\left[\cfrac{3.2 \times 10^6}{1.545 \times 10^3 \times .66 \times 10^3 \times 49 \times 10^4} - \cfrac{1}{700}\right]^2}$$

$$\left[\cfrac{3.2 \times 10^6}{1 + 1.545 \times 10^3 \times .66 \times 10^3 \times 7 \times 10^2}\right]^2$$

$$x\left[\cfrac{1}{49 \times 10^4} - \cfrac{3.2 \times 10^6}{1.545 \times 10^3 \times .66 \times 10^3 \times 49 \times 10^4 \times 7 \times 10^2}\right]$$

$$Cp-Cv = \cfrac{1.545 \times 10^3 \quad [1 + .004]^2}{.0045 \quad \left[\cfrac{1}{15.6 \times 10^4} - \cfrac{1}{7 \times 10^2}\right]^2}$$

$$x \left[\cfrac{1}{49 \times 10^4} - \cfrac{1}{109. \times 10^6}\right]$$

$$Cp-Cv = \cfrac{1.545 \times 10^3 \quad [1.01] \quad [.0204 \times 10^{-4} - .0092 \times 10^{-6}]}{[1.01-] \quad [.641 \times 10^{-4} - .143 \times 10^{-2}]^2}$$

$$= \cfrac{1.545 \times 10^3 \quad 2.03 \times 10^{-6}}{(-0.1374 \times 10^{-2})^2} = \cfrac{1545 \quad [2.03] \times 10^{-6}}{(1.37)^2 \times 10^{-6}}$$

$$= \cfrac{1545(2.03)}{1.88} = \cfrac{1668 \ ftlb}{1bmol\,^\circ R}$$

$$a = 1400 \ atm \ \cfrac{(ft^3)^2}{1bmol} \quad ; \quad b = 0.488 \ ft^3/1bmol$$

Van der Waals equation.

$$= 1400 \times 2116.2 \ \cfrac{1b}{ft^2} \ \cfrac{(ft^3)^2}{1bmol} = 2.96 \times 10^6 \ \cfrac{1b}{ft^2} \ \cfrac{(ft^3)^2}{1bmol}$$

$$T = 200^\circ F = 660^\circ R; \quad v = 38.85 = 700 \ \cfrac{ft^3}{1bmol}$$

$$R = 1545 \; \frac{\text{ftlb}}{\text{lbmol}^\circ R} \qquad p = 10 \text{ psia} = 1440 \; \frac{\text{lb}}{\text{ft}^2} \text{ abs.}$$

Cp-Cv for the Van der Waals at this point will be calculated first.

$$Cp\text{-}Cv = R^2 \left[ \frac{T^{1/2}}{p + \dfrac{a}{v^2} - \dfrac{2a(v-b)}{v^3}} \right]^2 \left[ \frac{RTv^3 - 2a(v-b)^2}{v^3(v-b)^2} \right]$$

$$= (1.545)^2 \times 10^6 \left[ \frac{660^{1/2}}{1440 + \dfrac{2.96 \times 10^6}{(7.)^2 \times 10^4} - \dfrac{2(2.96 \times 10^6)(7. \times 10^2)}{7^3 \times 10^6}} \right]^2$$

$$\times \left[ \frac{1.545 \times 10^3 \times 6.6 \times 10^2 \times 7^3 \times 10^6 - 2(2.96 \times 10^6)7^2 \times 10^4}{7^3 \times 10^6 \times 7^2 \times 10^4} \right]$$

$$= 2.39 \times 10^6 \left[ \frac{660^{1/2}}{1440 + \dfrac{296}{49} - \dfrac{6 \times 10^6}{49 \times 10^4}} \right]^2$$

$$\left[ \frac{350.0 \times 10^{12} - 300 \times 10^{10}}{17,500 \times 10^{10}} \right] = 2.39 \times 10^6 \left[ \frac{660^{1/2}}{1440 + 6.05 - 12.2} \right]^2$$

$$\left[ \frac{347}{175} \right] = 2.39 \left[ \frac{660}{(1436)^2} \right] \qquad \left[ \frac{347}{175} \right] \times 10^6 = \frac{2.18 \times 10^6}{1.436 \times 10^3} \; \frac{\text{ftlb}}{\text{lbmol}^\circ R}$$

$$= 1518 \; \frac{\text{ftlb}}{\text{lbmol}^\circ R}$$

Cp-Cv for the Callendar equation for superheated steam at these same conditions is:

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$$Cp-Cv = RT^2 \left[ \frac{RT^{\frac{13}{3}} + \frac{10}{3} pa}{pT^{\frac{13}{3}} \left(v-b + \frac{a}{T^{\frac{10}{3}}}\right)} \right]^2$$

$$Cp-Cv = 1545(660)^2 \left[ \frac{1545(660)^{\frac{13}{3}} + \frac{10}{3}(1440)(2.96 \times 10^6)}{1440(660)^{\frac{10}{3}} \left(700 - 0.488 + \frac{2.96 \times 10^6}{(660)^{\frac{10}{3}}}\right)} \right]^2$$

$$Cp-Cv = 1.545 \times (6.6)^2 \times 10^7 \left[ \frac{1.545 \times 10^3 (.66)^{\frac{13}{3}} \times (10^3)^{\frac{13}{3}} + 1.44 \times 10^{10}}{1.440 \times 10^3 (.66)^{\frac{13}{3}} \times (10^3)^{\frac{10}{3}} \left(7 \times 10^2 + \frac{2.96 \times 10^6}{(.66)^{\frac{10}{3}} \times (10^3)^{\frac{10}{3}}}\right)} \right]^2$$

$$Cp-Cv = 1.545 \times (6.6)^2 \times 10^7 \left[ \frac{0.2558 \times 10^{16} + 1.44 \times 10^{10}}{0.2385 \times 10^{16} (7 \times 10^2 + 18 \times 10^{-4})} \right]^2$$

$$Cp-Cv = 1545 \times (6.6)^2 \times 10^4 \left[ \frac{0.2558 \times 10^{16}}{1.6506 \times 10^{18}} \right]^2$$

$$Cp-Cv = 1545 \times 43.6 \times 10^4 [0.1545]^2 \times 10^{-4}$$

Cp-Cv = 1545 x 43.6 x 0.0239 = 1545 x 1.04

$$= 1610 \ \frac{ftlb}{lbmol^\circ R}$$

$$Cp-Cv = R = 1545 \ \frac{ftlb}{lbmol^\circ R} = \underline{constant \ for \ ideal \ gas.}$$

To see how closely these gas equations represent superheated steam, we will take two points for each gas to determine the change in entropy for a reversible, isothermal expansion of steam.

From the equation for the change in entropy as a function of two thermodynamic variables, we get:

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \quad and \quad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial T}\right)_v dv. \quad For \ a \ reversible \ isothermal:$$

$$dT = 0 \quad so \quad ds = \left(\frac{\partial p}{\partial T}\right)_v dv.$$

$$\left(\frac{\partial p}{\partial T}\right)_v \ \underline{for \ a \ Van \ der \ Waals \ equation:} \quad p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left[\frac{\partial \left(\frac{RT}{v-b} - \frac{a}{v^2}\right)}{\partial T}\right]_v = \frac{R}{v-b}$$

$$\underline{Callendar \ equation:} \quad p = \frac{RT}{v-b + \frac{a}{T^n}}$$

$$\left[\frac{\partial \left(\dfrac{RT}{v-b+\dfrac{a}{T^n}}\right)}{\partial T}\right]_v = \frac{\left(v-b+\dfrac{a}{T^n}\right)R - (RT)\left(\dfrac{-na}{T^{n+1}}\right)}{\left(v-b+\dfrac{a}{T^n}\right)^2}$$

Dieterici equation: $\quad p = \dfrac{RT}{v-b}\, e^{\frac{-a}{RTv}}$

$$\left[\frac{\partial \left(\dfrac{RT\, e^{\frac{-a}{RTv}}}{v-b}\right)}{\partial T}\right]_v = \frac{R}{v-b}\left[Te^{\frac{-a}{RTv}}\left(\frac{a}{RTv^2}\right) + e^{\frac{-a}{RTv}}\right] = \frac{Re^{\frac{-a}{RTv}}}{v-b}\left[\frac{a}{RvT} + 1\right]$$

perfect gas: $\quad pv = RT \qquad p = \dfrac{RT}{v}$

$$\left(\frac{\partial \left(\dfrac{RT}{v}\right)}{\partial T}\right)_v = \frac{R}{v}$$

Berthelot equation: $\quad p = \dfrac{RT}{v-b} - \dfrac{a}{Tv^2}$

$$\left[\frac{\partial \left(\dfrac{RT}{v-b} - \dfrac{a}{Rv^2}\right)}{\partial T}\right]_v = \frac{R}{v-b} + \frac{a}{T^2 v^2}$$

$ds = \dfrac{(R)}{v-b}\, dv$ $\quad$ Van der Waals equation:

$$ds = \left( \frac{(v-b + \frac{a}{T^n}) R + \frac{RTna}{T^{n+1}}}{(v-b + \frac{a}{T^n})^2} \right) dv = \frac{Rdv}{(v-b + \frac{a}{T^n})} + \frac{RT \ na \ dv}{T^n + 1(v-b + \frac{a}{T^n})^2}$$

<u>Callendar's equation.</u>

## <u>Dieterici</u>

$$ds = \frac{Re^{\frac{-a}{RTv}}}{v-b} \left[ \frac{a}{RvT} + 1 \right] \qquad dv = \frac{a \ dv}{e^{\frac{a}{RTv}}(v-b)vT} + \frac{R \ dv}{e^{\frac{a}{RTv}}(v-b)}$$

$$ds = \frac{R}{v} \ dv \ \text{perfect gas}$$

$$ds = \frac{(R)}{v-b} \ dv + \frac{a}{T^2 v^2} \ dv \ \underline{\text{Berthelot's equation.}}$$

To get the change in entropy, we will integrate the equations for $s_2 - s_1$.

$$\int_{s_1}^{s_2} ds = \int_{v_1}^{v_2} \frac{R}{v-b} \ dv = R \left[ \ln(v-b) \right]_{v_1}^{v_2} = R \left[ \ln(v_2-b) - \ln(v_1-b) \right]$$

$$= R \left[ \ln \frac{(V_2-b)}{(V_1-b)} \right] \ \text{Van der Waals}$$

$$\int_{s_1}^{s_2} ds = R \int_{v_1}^{v_2} \frac{dv}{v-b+\frac{a}{T^n}} + R\frac{Tna}{T^{n+1}} \int_{v_1}^{v_2} \frac{dv}{\left( v-b+\frac{a}{T^n} \right)^2} = R \left[ \ln(v-b+\frac{a}{T^n}) \right]_{v_1}^{v_2} +$$

$$\frac{RTna}{T^{n+1}} \left[ \frac{1}{-2+1} \left(v-b + \frac{a}{T^n}\right)^{-2+1} \right]_{v_1}^{v_2} =$$

$$R \left\{ \ln\left(\frac{v_2-b+\frac{a}{T^n}}{v_1-b+\frac{a}{T^n}}\right) - \frac{Tna}{T^{n+1}} \left(\frac{1}{v-b+\frac{a}{T^n}}\right)\right\}_{v_1}^{v_2}$$

$$\int_{s_1}^{s_2} ds = R \left\{ \ln\left(\frac{v_2-b+\frac{a}{T^n}}{v_1-b+\frac{a}{T^n}}\right) - \frac{Tna}{T^{n+1}} \left[\frac{1}{v_2-b+\frac{a}{T^n}} - \frac{1}{v_1-b+\frac{a}{T^n}}\right]\right\}$$

$$= R \left\{ \ln\left(\frac{v_2-b+\frac{a}{T^n}}{v_1-b+\frac{a}{T^n}}\right) + \frac{Tna}{T^{n+1}} \left[\frac{1}{v_1-b+\frac{a}{T^n}} - \frac{1}{v_2-b+\frac{a}{T^n}}\right]\right\}$$

Callendar's equation.

$$\left[\frac{\partial \left(\frac{RT\,e^{\frac{-a}{RTv}}}{v-b}\right)}{\partial T}\right]_v = \frac{R}{v-b} \left[Te^{\frac{-a}{RTv}} \left(+\frac{a}{RvT^2}\right) + e^{\frac{-a}{RTv}}\right]$$

$$= \frac{Re^{\frac{-a}{RTv}}}{v-b} \left[\frac{a}{RTv} + 1\right]$$

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$$\int_{v_1}^{v_2} \frac{Re^{\frac{-a}{RTv}}}{v-b} \left[\frac{a}{RTv} + 1\right] \, d = \int_{s_1}^{s_2} ds$$

$$= \frac{Re^{\frac{-a}{RTv}}}{(v-b)} \frac{a \, dv}{RTv} + \frac{Re^{\frac{-a}{RTv}}}{v-b} \, dv$$

$$V = \frac{a}{RTx}$$

let $\frac{a}{RTv} = x$

$$dx = \frac{-a}{RTv^2} \, dv$$

$$dv = -\frac{RTv^2}{a} \, dx$$

$$\frac{ae^{-x} RTv^2}{Tav(v-b)} \, dx + \frac{Re^{-x}(-RTv^2 \, dx)}{(v-b) \, a}$$

$$\frac{Re^{-x} v dx}{(v-b)} - \frac{R^2T \, e^{-x} \, vdx}{a}$$

let $v-b = v$
where $v \gg b$

$$Re^{-x} dx - \frac{R^2Te^{-x}a \, dx}{a \quad RTx}$$

$$\int_{v_1}^{v_2} Re^{-x} dx - \frac{Re^{-x} dx}{x}$$

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$$R\left[\int_{v_1}^{v_2} e^{-x}\,dx - \int_{v_1}^{v_2} \frac{e^{-x}dx}{x}\right] =$$

$$R\left[-e^{-x} - \left[\ln x - x + \frac{(-x)^2}{2\cdot 2!} + \frac{(-x)^3}{3\cdot 3!}\right]_{v_1}^{v_2}\right] =$$

$$R\left[-e^{\frac{-a}{RTv}} - \left[\ln \frac{a}{RTv} - \frac{a}{RTv} + \frac{\left(\frac{-a}{RTv}\right)^2}{2\cdot 2!} + \frac{\left(\frac{-a}{RTv}\right)^3}{3\cdot 3!} + \cdots\right]_{v_1}^{v_2}\right] =$$

$$R\left[\frac{a}{RTv} + \frac{\left(\frac{a}{RTv}\right)^3}{3\cdot 3!} - e^{\frac{-a}{RTv}} - \ln \frac{a}{RTv} - \frac{\left(\frac{a}{RTv}\right)^2}{2\cdot 2!}\right]_{v_1}^{v_2} =$$

$$R\left\{\left[\frac{a}{RTv_2} + \frac{\left(\frac{a}{RTv_2}\right)^3}{3\cdot 3!} - e^{\left(\frac{-a}{RTv_2}\right)} - \ln \frac{a}{RTv_2} - \frac{\left(\frac{a}{RTv_2}\right)^2}{2\cdot 2!}\right.\right.$$
$$\left.\left. - \frac{a}{RTv_1} + \frac{\left(\frac{a}{RTv_1}\right)^3}{3\cdot 3!} - e^{\frac{-a}{RTv_1}} - \ln \frac{a}{RTv_1} - \frac{\left(\frac{a}{RTv_1}\right)^2}{2\cdot 2!}\right]\right\} =$$

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$$R\left[\frac{a}{RTv_2} + \frac{\left(\dfrac{a}{RTv_2}\right)^3}{3\cdot 3!} - e^{\frac{-a}{RTv_2}} \quad \ln\frac{a}{RTv_2} - \left(\frac{a}{RTv_2}\right)^2 - \frac{a}{RTv_1}\right.$$

$$\left. - \frac{\left(\dfrac{a}{RTv_1}\right)^3}{3\cdot 3!} + e^{\frac{-a}{RTv_1}} + \ln\frac{a}{RTv_1} + \frac{\left(\dfrac{a}{RTv}\right)^2}{2\cdot 2!}\right]$$

$$\int_{s_1}^{s_2} ds = R\int_{v_1}^{v_2}\frac{dv}{v} = R\ln\frac{v_2}{v_1} \qquad \underline{\text{Perfect gas.}}$$

$$\int_{s_1}^{s_2} ds = \int_{v_1}^{v_2}\frac{R\,dv}{v-b} + \frac{a}{T^2}\int\frac{dv}{v^2} = R\left[\ln(v-b)\right]_{v_1}^{v_2} + \left[\frac{a}{T^2(-v)}\right]_{v_1}^{v_2}$$

$$= R\left\{\ln\frac{(v_2-b)}{(v_1-b)}\right\} - \frac{a}{T^2v_2} + \frac{a}{T^2v_1} \qquad \underline{\text{Berthelot's equation.}}$$

The two points used for the test for four of these gases will show how closely each represents the change in entropy of superheated steam. The first will be:

temperature$_1$ = $\underline{6}$00°F = 1060°R;   pressure$_1$ = 1200 psia =

173,000$\dfrac{\text{lb}}{\text{ft}^2}$ ;  $v_1$ = 0.4016 = 7.5$\dfrac{\text{ft}^3}{\text{lbmol}}$

The second point will be: temp = 600°F = 1060°R;

pressure$_2$ = 20 psia = 2880 lb/ft$^2$ ; $v_2$ = 31.47 = 626 ft$^3$/lbmol

<u>Van der Waals' equation:</u>  $s_2 - s_1 = R\ \ln\dfrac{(626 - 0.488)}{7.5 - 0.488}$

$$s_2 - s_1 = 1545 \ln \frac{(625.512)}{7.012} = 1545 \times \ln (89.05)$$

$$s_2 - s_1 = 1545 \times 4.485 = 6930 \frac{ftlb}{lbmol}$$

Callendar's equation:

$$s_2 - s_1 = R \left\{ \ln \frac{v_2 - b + \frac{a}{T^n}}{v_1 - b + \frac{a}{T^n}} + \frac{Tna}{T^{n+1}} \left[ \frac{1}{v_1 - b + \frac{a}{T^n}} - \frac{1}{v_2 - b + \frac{a}{T^n}} \right] \right\}$$

where $a = 1.53 \times 10^{10}$   $b = -0.55$

$$s_2 - s_1 = R \left\{ \ln \left( \frac{626 + .55 + \frac{1.53 \times 10^{10}}{(1.06 \times 10^3)^{\frac{13}{3}}}}{7.5 + .55 + \frac{1.53 \times 10^{10}}{(1.06 \times 10^3)^{\frac{10}{3}}}} \right) + \frac{1060(10) \, 1.53 \times 10^{10}}{3 \, (1.06 \times 10^3)^{\frac{13}{3}}} \right.$$

$$\left. \left[ \frac{1}{7.5 + 0.55 + \frac{1.53 \times 10^{10}}{(1.06)^{\frac{10}{3}} 10^{10}}} - \frac{1}{626 + .55 + \frac{1.53 \times 10^{10}}{(1.06^{\frac{10}{3}}) 10^{10}}} \right] \right\}$$

$$s_2 - s_1 = R \left\{ \ln \frac{(626.55 + 1.26)}{8.05 + 1.26} + 4.44 \left[ \frac{1}{9.31} - \frac{1}{627.81} \right] \right\}$$

$$s_2 - s_1 = R \{4.21 + 0.476\} = 1545 \{4.686\}$$

$$s_2 - s_1 = 7240 \frac{ftlb}{lbmol}$$

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$$\frac{a}{RTv_1} = \frac{3.2 \times 10^6}{1.545 \times 10^3 \times 1.06 \times 10^3 (7.5)} = 0.26 \quad \underline{\text{Dieterici's equation.}}$$

$$\frac{a}{RTv_2} = \frac{0.26v_1}{v_2} = \frac{0.26 \times 7.5}{626} = 0.0031$$

$$s_2 - s_1 = 1545 \left[ .0031 - \frac{1}{e^{.0031}} - \ln(.0031) - 0.26 \right.$$

$$\left. + \frac{1}{e^{.26}} + \ln(.26) + .015 \right]$$

$$s_2 - s_1 = 1545 \left[ .0031 - 1 + 5.76 - .26 + 1.3 - 1.345 + .015 \right]$$

$$s_2 - s_1 = 1545 \times 4.47 = 6900 \ \frac{\text{ftlb}}{\text{lbmol}}$$

<u>Perfect gas:</u>

$$s_2 - s_1 = R \ \ln \frac{v_2}{v_1} = 1545 \times \ln \frac{626}{7.5} = 1545 \times 4.42$$

$$s_2 - s_1 = 6830 \ \frac{\text{ftlb}}{\text{lbmol}}$$

<u>Berthelot's equation:</u> $\quad b = 0.302; \quad a = 8.14 \times 10^8 \ \frac{\text{lb}}{\text{ft}^2} \ \left( \frac{\text{ft}^3}{\text{lbmol}} \right)^2 {}^\circ R$

$$s_2 - s_1 = R \ \ln \frac{(v_2 - b)}{v_1 - b} - \frac{a}{T^2 v_2} + \frac{a}{T^2 v_1}$$

$$s_2 - s_1 = 1545 \ \ln \frac{(626 - .302)}{7.5 - .302} - \frac{8.14 \times 10^8}{(1.06)^2 \times 10^6 \times 6.26 \times 10^2}$$

$$+ \frac{8.14 \times 10^8}{(1.06)^2 \times 10^6 \times 7.5}$$

$$s_2 - s_1 = 6900 - 1.158 + 0.967 \times 10^2$$

$$= 6900 + 95.5 = 6995.5 \; \frac{ftlb}{lbmol}$$

From the steam tables by Keenan and Keys, "Thermodynamic properties of Steam," we obtain the actual change in entropy of the two states. Entropy at 20 psia and 600°F = 1.940, and entropy at 1200 psia and 600°F = 1.410 Btu/lb. This is equal to 1.940 - 1.410 = 0.53 Btu/lb.

In $\frac{ftlb}{lbmol}$ , this is 0.53 x 18 x 778.3 = 7410 $\frac{ftlb}{lbmol}$ .

The variation for each gas equation is shown in Figures 1 and 2.

The percentage deviation for each is as follows: $\underline{\text{actual-calc.}}$
$$\text{actual}$$

Van der Waals - $\frac{7410-6930}{7410} = \frac{480}{7410}$ x 100% = 6.48%

Callendar - $\frac{7410-7240}{7410}$ = 2.29%

Dieterici - $\frac{7410-6900}{7410}$ = 6.87%

Perfect gas - $\frac{7410-6830}{7410}$ = 7.83%

Berthelot - $\frac{7410-6996}{7410}$ = 5.60%

It is obvious that, of these cases considered, the Callendar equation describes superheated steam best. The same could be done for other gasses to determine which equation would fit them best.

III. CONCLUSIONS

It can be seen that the differences and ratios of specific heats and change in entropy may be determined for the considered five equations of state.

Comparisons of the difference in specific heats and change in entropy for superheated steam at a few selected points show that these equations fit the actual case fairly well, and most of the equations are useable for engineering calculations.

These reduced equations could be used to establish useful engineering design tables for several frequently considered gases.
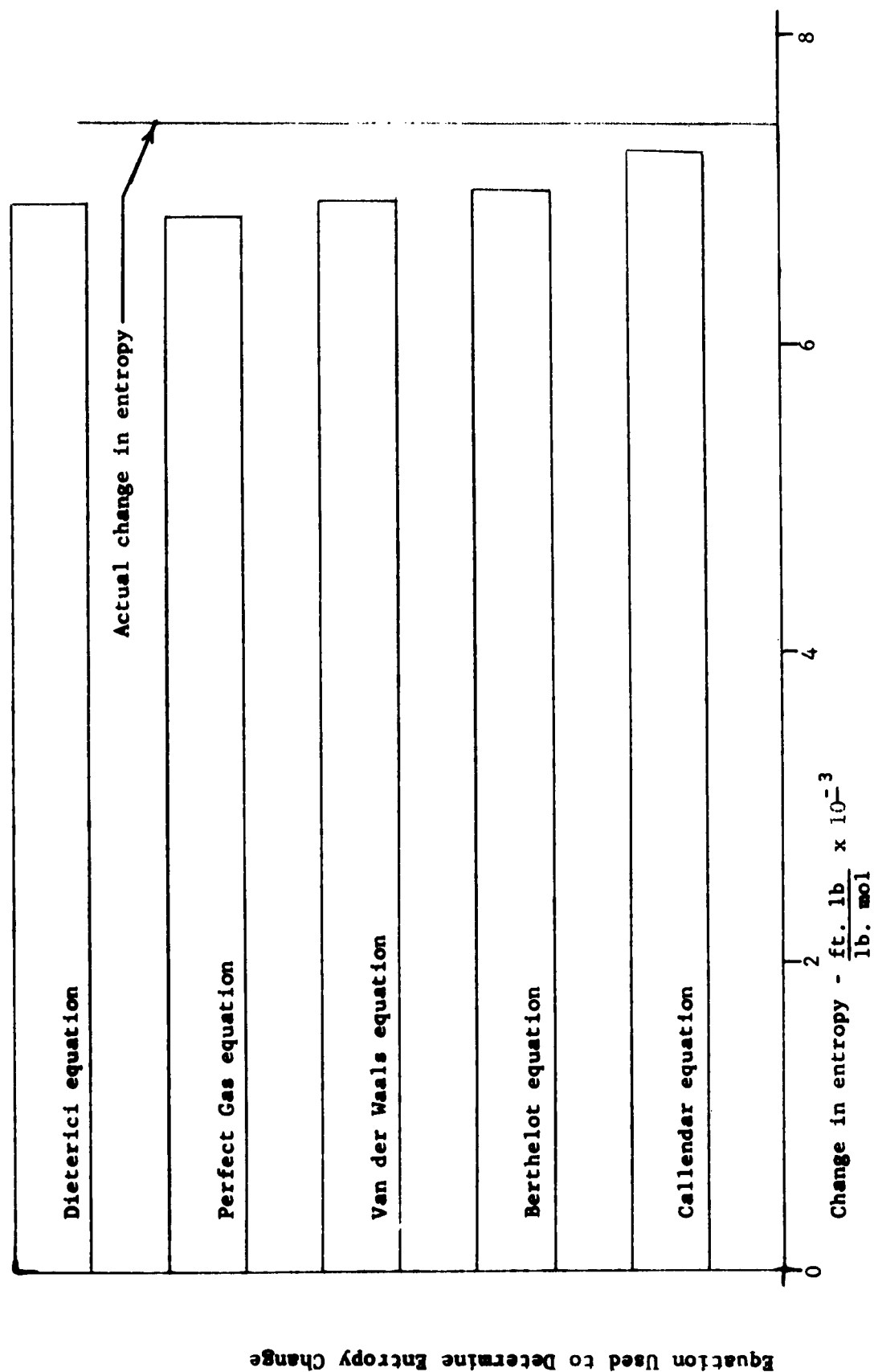
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Figure 1. CHANGE IN ENTROPY OF SUPERHEATED STEAM CALCULATED FOR FIVE GAS EQUATIONS. T=600°F CONSTANT
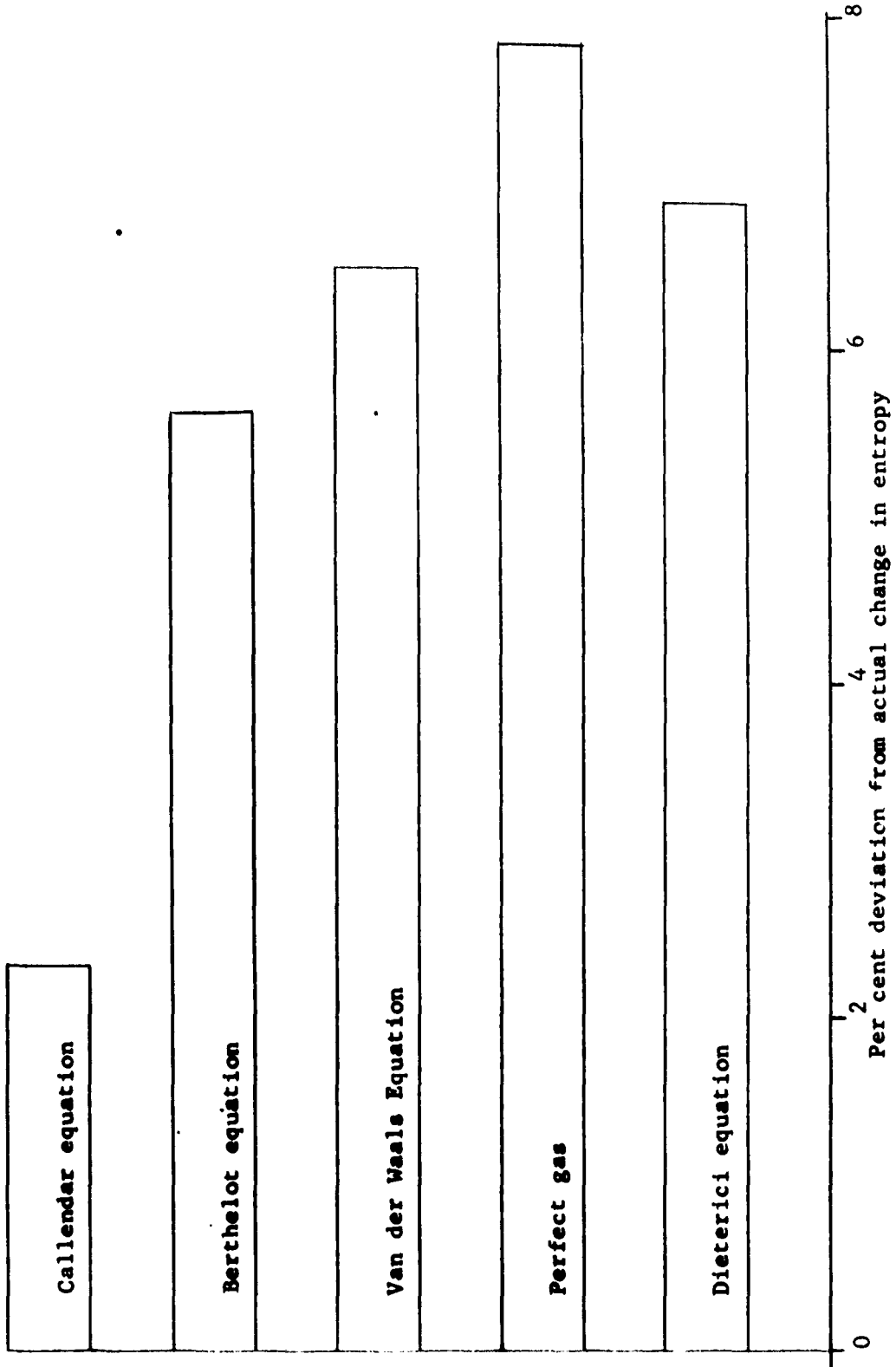
Figure 2. PERCENT DEVIATION FROM ACTUAL CHANGE IN ENTROPY FOR SUPERHEATED STEAM FOR FIVE GAS EQUATIONS. T=600°F.
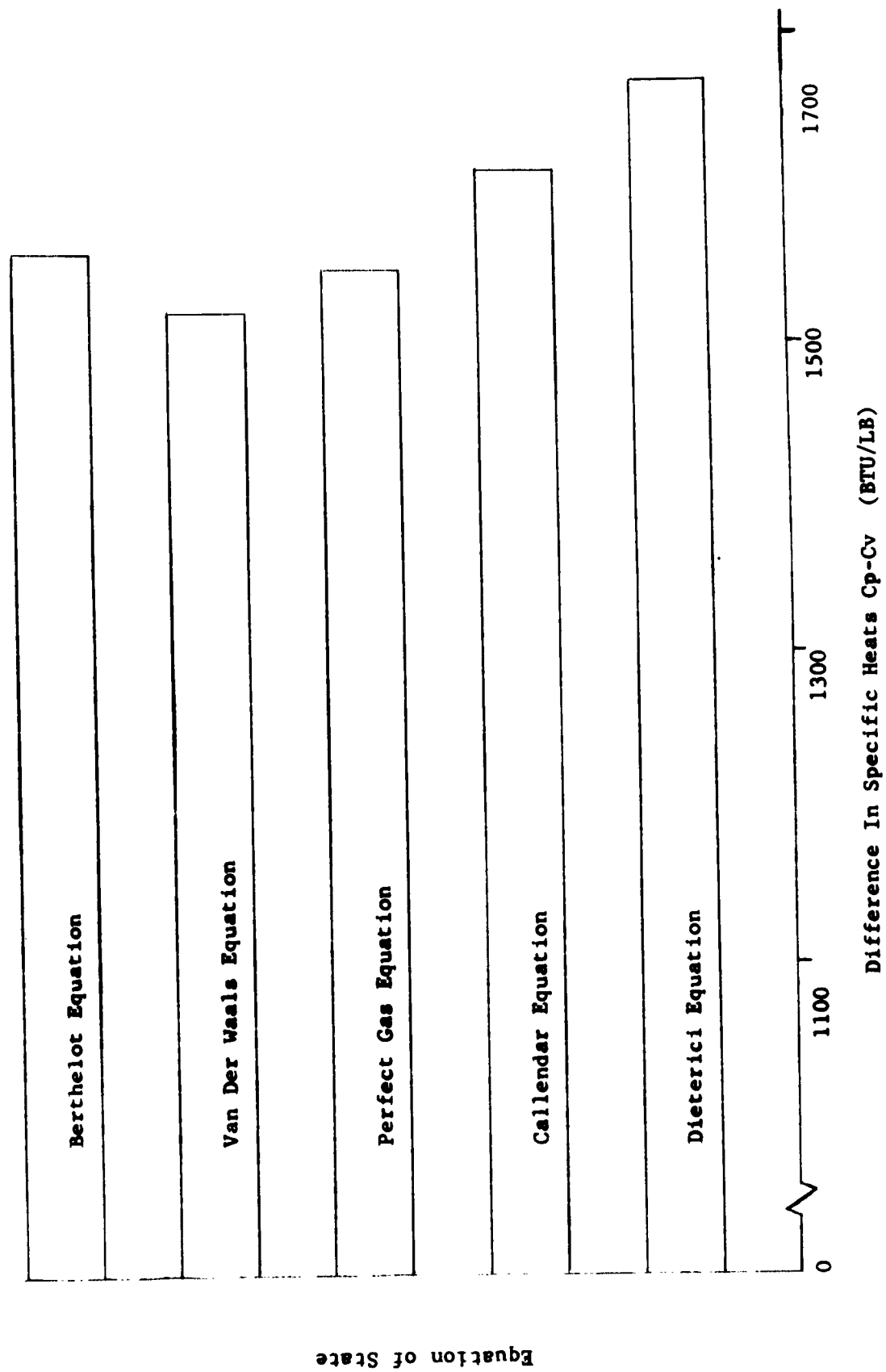
Figure 3. CALCULATED DIFFERENCES IN SPECIFIC HEATS FOR SUPERHEATED STEAM FROM FIVE EQUATIONS OF STATE.

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